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Laser-induced synthesis of carbon-based electrode materials for non-enzymatic glucose detection

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Abstract
We report one-step synthesis of carbon-based microstructures on the surface of polyimide by using the 2D direct laser writing technique. It was shown that the properties of obtained conductive structures can be tuned by varying the conditions of the laser synthesis (scanning speed, laser power). The fabricated materials exhibited high electrochemical activity towards D-glucose measured by cyclic voltammetry analysis (limit of detection—0.564 μM and 6.31 μM for different linear ranges). Comparatively high sensing activity of the synthesized structures makes them promising materials for flexible non-enzymatic biosensing devices.

Keywords Direct laser writing · Flexible electrodes · Non-enzymatic sensors · Polyimide

1 Introduction

With the modern rate of informatization and development of Internet of Things and cloud storage technologies (Aleeva et al. 2018) conventional silicon-based devices are not capable to meet all new emerging requirements (Tao et al. 2017; Ye et al. 2017). In the last decade the different applications of wearable and flexible electronics are drawing more and more interest of the academic society as well as industry (Wang et al. 2018). For instance, in a field of medicine and healthcare such devices can collect and analyze a number of essential indicators like heart rate, body temperature, level of glucose and lactose in real time (Shiwaku et al. 2018; Oh et al. 2018). The development of flexible and wearable skin-interfaced monitoring device aims to analyze such biological liquids as sweat, tears and saliva in addition to blood. This approach allows to perform non-invasive analysis with no disturbance of outer protective layers of the skin and contact with the blood, therefore

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the risk of infectioning becomes minimized and the convenience is significantly increased (Kim et al. 2019).

The perspective materials for flexible sensors are carbon-based materials, such as graphene, graphene oxide (GO), reduced graphene oxide (rGO), etc. because of their outstanding physicochemical properties (Zhang et al. 2010; Kumar et al. 2016; Khalili Sadaghiani et al. 2019). For instance, the family of 2D graphene-related materials has been proven to have great potential in the field of voltammetric biosensors (Tiwari et al. 2016).

Previously many synthetic routes to carbon materials, particularly graphene, have involved the use of toxic precursors, such as hydrazine (as reducing agent) (Gao et al. 2010) or high temperatures (in case of thermal reduction) (Larciprete et al. 2011). Such severe fabrication conditions are the serious obstacle for subsequent technological stages of device production. This fact has led to the development of advanced, simple and green synthetic approaches. One of the promising techniques is the direct laser writing (DLW) (Kumar et al. 2017; Panov et al. 2016; Baranauskaite et al. 2019). DLW process has a number of advantages in comparison with other aforementioned methods of graphene synthesis among them the absence of the necessity to use a catalyst, non toxicity, being contactless. Moreover, laser-assisted approach make it possible to synthesize different kind of materials either in the ambient air or in a solution at room temperature by very precise local influence on the substrate within the microreactor in focal point of beam (Shishov et al. 2019; Smikhovskaia et al. 2018; Mizoshiri et al. 2019). This helps to minimize possible side effects, which can take place during the fabrication of flexible sensors. The possibility of laser pyrolytic carbonation of thin polymer films was shown for wide range of materials, for instance poly(methyl methacrylate) (PMMA), polyethylene terephthalate (PET), polyethylene (PE), polycarbonates (PC), polytetrafluoroethylene (PTFE), polyamide and polyimide (PI) (Ghoniem et al. 2016; Goodridge et al. 2012; Duy et al. 2018; Marengo et al. 2017).

In this article, we propose the one-step laser-induced fabrication of carbon-based electrode materials with high sensory activity towards D-glucose by localized surface modification of polyimide.

2 Experimental

2.1 Direct laser writing technique

The detailed description of the experimental setup for direct laser writing has been published elsewhere (Smikhovskaia et al. 2019). Briefly, the output from a continuous wave 532 nm diode-pumped solid-state Nd:YAG laser is divided into two portions, Fig. 1. The first portion is focused on a surface of the polymeric substrate (in this study 125 μm Kapton® Polyimide) mounted on motorized stage. In turn, the second portion of output is sent to the web-camera used for in situ monitoring the laser-induced process. Laser radiation power is controlled by the power meter LPM-905. Laser power and scanning speed are varied from 60 to 120 mW and from 0.25 to 1.1 mm s^{-1} respectively.

2.2 Characterization of the synthesized microstructures

The morphology of the synthesized microstructures was examined using scanning electron microscopy (SEM) with a Zeiss Supra 40 VP scanning electron microscope. Raman spectra were recorded on Raman spectrometer Senterra (Bruker) using a 488 nm laser.

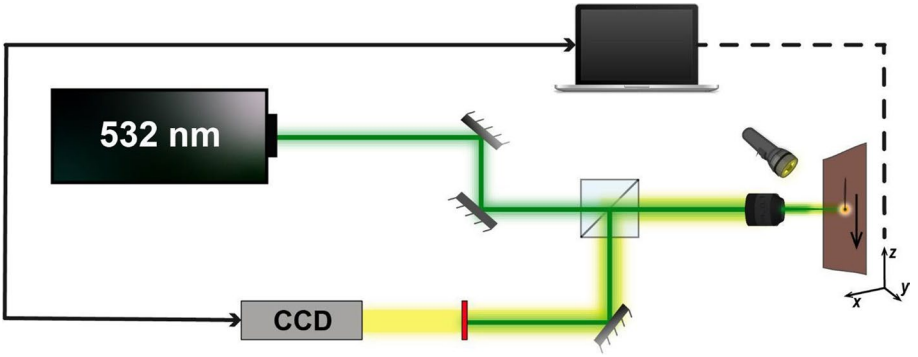

Fig. 1 The scheme of the experimental setup for direct laser writing of carbon-based microstructures on the surface of PI sheet

All electrochemical measurements were conducted at room temperature. Electrochemical properties of carbonaceous structures were studied by using cyclic voltammetry (potentiostat Elins P301). All measurements were conducted in a standard three-electrode electrochemical cell having a glass-like carbon electrode as an auxiliary electrode, an Ag/AgCl electrode (3.5 M KCl) as a reference electrode and synthesized microstructures as a working electrode, Fig. 2.

The scan rate of the potential was set at 50 mV s^{-1}. Measurements of electrochemical activity of the structures towards D-glucose were carried out in the solutions containing 0.1 M sodium hydroxide (NaOH) in a potential range from -0.2 V to 1 V. The solutions of D-glucose of different concentrations were added to the background solution with simultaneous stirring.

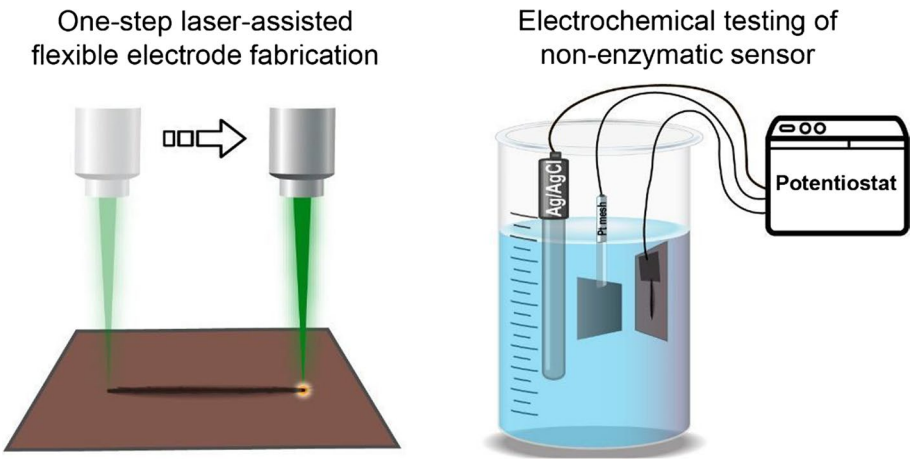

Fig. 2 Three electrodes electrochemical cell for testing electrocatalytic activity towards D-glucose

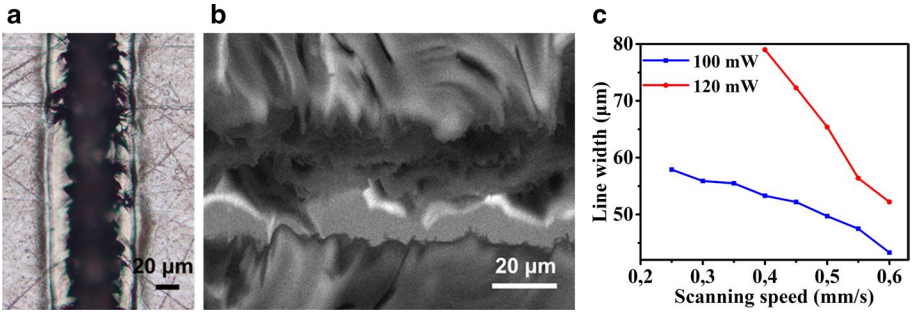

Fig. 3 **a** Optical micrograph, **b** SEM image of Kapton® polyimide after exposure to laser beam with power 100 mW and scanning speed 0.55 mm s^{-1} and **c** typical dependence of the structure width on scanning speed. (Color figure online)

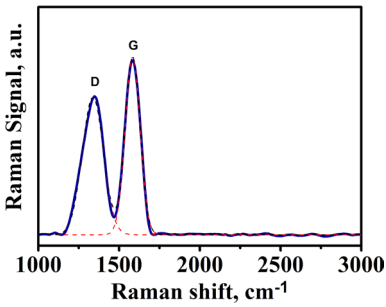

Fig. 4 Raman spectrum of the carbon-based structure fabricated by the laser irradiation of PI

3 Results and discussion

The synthesized carbon-based structures were investigated using optical microscopy and scanning electron microscopy (SEM), Fig. 3a, b. SEM-images shows formation of the gap with carbonated walls on PI film under laser radiation, such way of substrate modification allows to create sensors with pseudo 3D architecture. Morphology of the walls of the structure is similar to the graphene-based material obtained in (Marengo et al. 2017).

Figure 3c represents the typical dependence of laser power on the structure width, as it may be expected, the width is decreasing with lowering the laser fluence. Varying the laser power and scanning speed allows to tune the resolution of the direct laser writing process. The optimal size of microstructures for flexible sensor fabrication is determined by tendency to device miniaturization on the one hand and by surface tension of water-based medium on the other hand, too narrow structures may hinder the penetration of solution inside the gaps and therefore interfere with obtaining correct results of analysis.

Raman spectroscopy is a widely used and very helpful technique for nondestructive characterization of carbon-based materials. Raman spectra can provide information about their structure, as well as a quantification of the disorders and defects introduced by the laser irradiation. Typical Raman spectrum of fabricated structure, Fig. 4, reveals only two broad overlapping peaks at 1347 cm^{-1} (D band) and 1583 cm^{-1} (G band) and no second-order features, this kind of spectra may be assigned to graphene-like materials, graphene oxide in particular. The high ratio of intensity of D/G bands (Id/Ig = 1.1) indicates the

formation of highly defective carbon-based structures during the laser-induced synthesis (Wu et al. 2018; Muzyka et al. 2018). In addition, one can see, that there are no peaks corresponding to C–N or C=C vibrations (Raimondi et al. 2000), it confirms that the full carbonization of irradiated surface of PI substrate has occurred.

The conductive carbon-based structures were used as working electrodes for non-enzymatic glucose sensing. It is worth to mention that no extra treatment or preparation required after in air laser processing, therefore laser direct writing technique provides simple, waste-free and environmentally friendly approach to fabrication of electrode materials. The sensor properties of microelectrodes were examined by recording cyclic voltammograms in solutions containing different concentration of D-glucose, Fig. 5a. Figure 5b presents the voltammetric response of the proposed electrode after consecutive additions of D-glucose in 0.1 M NaOH at 0.3 V.

Figure 5b shows two linear regions of calibration curves:

$$\text{in the range of } 0-1.0\,\mu\text{M},\ j(\text{mA}) = 3.133 \times C(\mu\text{M}) + 1.415, \tag{1}$$

$$\text{in the range of } 1.0-10\,\mu\text{M},\ j(\text{mA}) = 0.222 \times C(\mu\text{M}) + 4.201, \tag{2}$$

Limit of detection (LOD) exhibited by carbon-based microelectrode was calculated using following equation: LOD = 3S/b, where S is the standard deviation of the signal and b is the slope of the calibration curve. The calculated limit of detection of D-glucose is 0.564 μM and the maximum sensitivity is 294.6 μA * μM^{-1} * cm^{-2} ($R^2 = 0.974$) for the first linear region (red line, Fig. 5b) and 6.31 μM and 252.3 μA * μM^{-1} * cm^{-2} ($R^2 = 0.968$) respectively for the second linear region (blue line, Fig. 5b). The decrease in sensitivity can be explained by the adsorption of intermediates formed during the glucose electrooxidation reaction, it leads to decreasing of available active sites on material surface and to slowing down the absorption of analyte at higher concentration (El Khatib and Abdel Hameed 2011).

The sensor parameters displayed by carbon-based microstructures synthesized by direct laser writing technique were compared with the same characteristics of several similar electrode materials known to date (Tables 1). Summarizing the obtained results one can conclude that the fabricated in this work microelectrodes exhibit better sensor properties

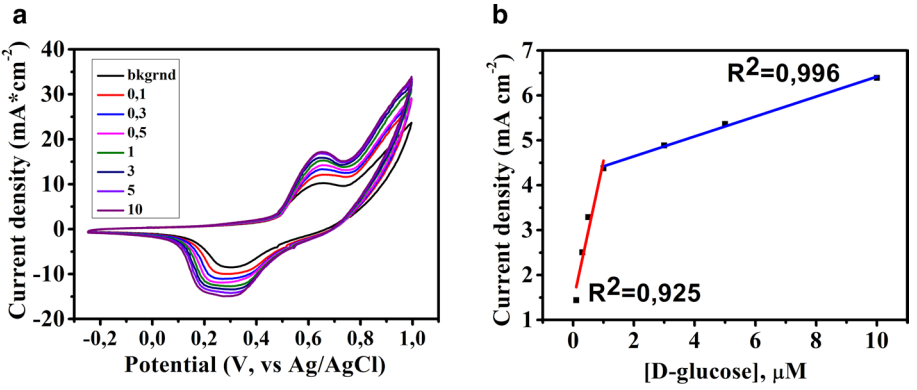

Fig. 5 **a** Cyclic voltammograms of carbon-based microelectrode recorded in solutions containing D-glucose. In legend concentrations of D-glucose are indicated in μM and **b** voltamperometric response of the microelectrode after consecutive additions of D-glucose. (Color figure online)

Table 1 The comparison of the sensor properties towards D-glucose exhibited by carbon-based microelectrode and other similar analogs

Type of electrode	Detection limit (mmol L^{-1})	Sensitivity (μA cm^{-2} mM^{-1})	Linear range (mmol L^{-1})	References
This work	0.006	252.37	0.001–0.01	–
This work	0.0006	294.63	0.0001–0.001	–
Ni-Co NSs/RGO/GCE	3.79	1773.61	0.01–2.65	Wang et al. (2013)
Cu-CoNSs	0.01	1171	0.015–1.21	Wang et al. (2014)
Graphene-Co_3O_4 nanoneedle electrode	< 10	–	0.05–0.3	Wang et al. (2012)
Cu nanocubes/MWCNTs	0.001	1096	Up to 7.5	Yang et al. (2010)

than many other analogs due to lower limit of detection, broader range of linearity, or higher sensitivity.

4 Conclusion

In this work, we produced electrocatalytically active carbon-based microstructures on surface of polyimide using a simple and cheap direct laser writing technique. Electrochemical measurements of the fabricated electrodes showed high sensitivity (252.3 μA * $μM^{-1}$ * cm^{-2}) and low LOD (6.31 μM) with respect to D-glucose. These results proved the DLW as promising approach for micropatterning and microelectrode fabrication.

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